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(21) International Application Number: PCT/IB96/00565 (22) International Filing Date: 7 June 1996 (07.06.96) (30) Priority Data: 7/166783 8 June 1995 (08.06.95) JP (71) Applicant (for all designated States except US): SUMITOMO METAL MINING COMPANY LIMITED [JP/JP]; 11-3, Shinbashi 5-chome, Minato-ku, Tokyo 105 (JP). (72) Inventors; and (75) Inventors/Applicants (for US only): URAGAMI, Yuji [JP/JP]; 18-5, Naka-kokubun 3-chome, Ichikawa-shi, Chiba 272 (JP). YAMAGUCHI, Eiji [JP/JP]; 18-5, Naka-kokubun 3-chome, Ichikawa-shi, Chiba 272 (JP). YOKOZUKA, Hideharu [JP/JP]; 18-5, Naka-kokubun 3-chome, Ichikawa-shi, Chiba 272 (JP). UEKUSA, Kikoo [JP/JP]; 18-5, Naka-kokubun 3-chome, Ichikawa-shi, Chiba 272 (JP). (74) Agent: MATSUI, Mitsuo; 3F, Nishishinbashi YS Building, 19-2, Nishishinbashi 2-chome, Minato-ku, Tokyo 105 (JP).	(81) Designated States: AL, AM, AT, AU, AZ, BB, BG, BR, BY, CA, CH, CN, CZ, DE, DK, EE, ES, FI, GB, GE, HU, IL, IS, JP, KE, KG, KP, KR, KZ, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, TJ, TM, TR, TT, UA, UG, US, UZ, VN, ARIPO patent (KE, LS, MW, SD, SZ, UG), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG). Published <i>With international search report.</i>	
(54) Title: HYDROTREATING CATALYST: COMPOSITION, PREPARATION, AND USE THEREOF		
(57) Abstract <p>The invention pertains to a process for activating a hydrotreating catalyst comprising a Group VIII hydrogenation metal oxide and a Group VI hydrogenation metal oxide on a carrier in which the hydrotreating catalyst is contacted with an additive which is at least one compound selected from the group of compounds comprising at least two hydroxyl groups and 2-10 carbon atoms, and the (poly)ethers of these compounds, after which the catalyst is dried under such conditions that at least 50 % of the additive remains in the catalyst. The additive, is preferably at least one compound selected from ethylene glycol, diethylene glycol, and polyethylene glycol, or a saccharide or polysaccharide. The invention additionally pertains to the catalyst obtainable by this process, which shows high activity in hydrodesulphurisation and hydrodenitrogenation reactions, and to the use of the catalyst in hydrotreating.</p>		

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HYDROTREATING CATALYST: COMPOSITION, PREPARATION, AND USE THEREOF

The invention relates to a catalyst composition suitable for hydrotreating, more particularly for hydrodesulphurisation and hydrodenitrogenation of hydrocarbon-containing feeds. The invention further relates to processes for the preparation and use of the catalyst composition.

In general, the object of catalytically hydrotreating hydrocarbon-containing feeds is the complete or partial removal of impurities. Common impurities are sulphur compounds and nitrogen compounds. The at least partial removal of such impurities from a feed will ensure that, when the final product is burnt, fewer sulphur oxides and/or nitrogen oxides harmful to the environment will be released. In addition, sulphur compounds and nitrogen compounds are toxic to many of the catalysts employed in the oil industry for converting feeds into ready-for-use products. Examples of such catalysts include cracking catalysts, hydrocracking catalysts, and reforming catalysts. It is therefore customary for feeds to be subjected to a catalytic hydrotreatment prior to their being processed in, say, a cracking unit.

Catalytic hydrotreatment implies contacting a feed with hydrogen at elevated temperature and pressure in the presence of a hydrotreating catalyst. In this process the sulphur compounds and nitrogen compounds present in the feed are converted into readily removable hydrogen sulphide and ammonia.

In general, hydrotreating catalysts are composed of a carrier with deposited thereon a Group VI metal component and a Group VIII metal component. The most commonly employed Group VI metals are molybdenum and tungsten, while cobalt and nickel are the conventional Group VIII metals. Phosphorus may also be present in the catalyst.

The prior art processes for preparing these catalysts are characterised in that a carrier material is composited with hydrogenation

metal components, for example by impregnation, after which the composite is calcined to convert the metal components into their oxides. Before being used in hydrotreating, the catalysts are generally presulphided to convert the hydrogenation metals into their sulphides.

Because the requirements as to the legally permitted sulphur and nitrogen contents in fuels are becoming ever stricter, there is a continuous need for hydrotreating catalysts with improved activity. Further, at a given final sulphur content a more active catalyst will make it possible to operate under milder process conditions (energy saving) or to increase the lifespan of a catalyst between regenerations (cycle length).

Various efforts have been made in the art to provide hydrotreating catalysts with improved activity. A relatively new trend in this field is the use of additives.

For example, Japanese patent application 04-166231 discloses a process for preparing a hydrotreating catalyst in which a support is impregnated with an impregnation solution comprising a Group VI metal component, a Group VIII metal component, and optionally a phosphorus component. The support is dried at a temperature of less than 200°C, contacted with a polyol, and then dried again at a temperature below 200°C.

Japanese patent application 04-166233 discloses substantially the same process as the above-mentioned patent application, except that instead of a polyol an alkoxycarboxylic acid is used.

Japanese patent application 06-339635 discloses a process in which a support is impregnated with an impregnation solution comprising an organic acid, Group VI and Group VIII hydrogenation metal components, and preferably a phosphorus component. The impregnated support is dried at a temperature below 200°C. The dried impregnated support is contacted with an organic acid or polyol, after which the

thus treated support is dried at a temperature below 200°C.

Japanese patent application 06-210182 discloses a process for preparing a catalyst in which a boria-alumina support comprising 3-15 wt.% of boria is impregnated with an impregnation solution comprising a Group VI metal component, a Group VIII metal component, and a polyol. The impregnated support is dried at a temperature of 110°C to form a catalyst.

European patent application 0 601 722 describes a process for preparing a catalyst in which a gamma-alumina support is impregnated with an impregnation solution comprising a Group VI metal component, a Group VIII metal component, phosphoric acid, water, and diethylene glycol. The impregnated support is dried at a temperature of 100°C. The catalysts are presulphided with a Kuwait straight-run gas oil containing 1.15 wt.% of sulphur and 3% butane thiol.

Although these catalysts do indeed show improved hydrotreating activity as compared with conventional hydrotreating catalysts which do not contain an additive, this improved activity will only appear when the catalyst is used for the first time. Regeneration of the catalyst by burning off coke results in removal of the additive from the catalyst, so that the improvement in activity is lost in the further catalyst life cycles.

The present invention now relates to a process for preparing a hydrotreating catalyst which is also suitable for activating hydrotreating catalysts which were either prepared in a conventional manner without the use of an additive, or from which the additive was removed by regeneration.

The process according to the invention is characterised in that a hydrotreating catalyst comprising a Group VIII hydrogenation metal oxide and a Group VI hydrogenation metal oxide on a carrier is contacted with an additive which is at least one compound selected from the group of compounds comprising at least two hydroxyl groups and 2-10 carbon atoms, and the (poly)ethers of these compounds,

after which the catalyst is dried under such conditions that the additive substantially remains in the catalyst.

5 The hydrotreating catalyst used as starting material in the process according to the invention may thus be a conventional hydrotreating catalyst prepared by a process in which hydrogenation metal components are composited with a carrier, after which the composite material is subjected to a calcination step to convert the hydrogenation metal components into their oxides. However, the hydrotreating catalyst used as starting material may also be a used
10 hydrotreating catalyst from which the additive, if there was one, was removed by regeneration after the catalyst's first use.

It should be noted that US 4,530,917 describes a process in which a conventional hydrotreating catalyst is contacted with an additive,
15 but in this patent the additive is present in a presulphiding solution which contains a polysulphide as sulphiding agent. By contrast, in the process according to the invention the impregnation solution does not contain a sulphiding agent. Further, it was found that the catalyst prepared by the process according to the invention
20 has such high activity that presulphiding can often be dispensed with.

It should further be noted that US 5,032,565 describes a process for reducing catalysts comprising a Group VIII metal by contacting them with a reducing agent which may be an alcohol or polyalcohol. It is
25 expressly stated that this process is applicable to catalysts which normally are not sulphided because sulphur is a poison to this type of catalyst. By contrast, the catalysts of the present invention are of the type which is not poisoned by sulphur compounds and is often sulphided before or during use.

30 The present invention also relates to catalysts which can be obtained by the process described above. Thus, the present invention also relates to a hydrotreating catalyst comprising a Group VIII

metal oxide and a Group VI metal oxide on a carrier, which catalyst additionally comprises an additive which is at least one compound selected from the group of compounds comprising at least two hydroxyl groups and 2-10 carbon atoms, and the (poly)ethers of these compounds, wherein the Group VIII metal compound and the Group VI metal compound are in the form of oxides.

As has been explained earlier, before conventional hydrotreating catalysts are used in the hydrotreating of hydrocarbon feeds, they are generally subjected to a sulphidation treatment to convert the metal oxides into metal sulphides. This sulphidation treatment can be carried out by contacting the catalyst with hydrogen sulphide at elevated temperature and pressure, with elemental sulphur, or with an organic sulphur compound such as a polysulphide. It is also possible to sulphide the catalyst by contacting it with a hydrocarbon feed to which additional sulphur compounds have been added (spiked hydrocarbon feed). Needless to say, it would be a major advantage if a catalyst were available which would have high activity without requiring a presulphidation step with a separate presulphiding agent or a spiked feed. It has now been found that the catalyst according to the invention shows such high activity. For the catalyst according to the invention it is sufficient to be contacted with the feed to be hydrotreated if said feed contains at least 0.2 wt.% of sulphur. This makes it possible to use the catalyst according to the invention without a separate sulphiding step using additional sulphur compounds being necessary, even if the sulphur content of the feed is as low as 0.2 wt.%.

Accordingly, the present invention also relates to a process for hydrotreating a hydrocarbon feed in which a hydrocarbon feed which contains at least 0.2 wt.% of sulphur is contacted under conditions of elevated temperature and pressure with a hydrotreating catalyst comprising a Group VIII metal oxide and a Group VI metal oxide on a carrier, which catalyst additionally comprises an additive which is

at least one compound selected from the group of compounds comprising at least two hydroxyl groups and 2-10 carbon atoms, and the (poly)ethers of these compounds, wherein the Group VIII metal compound and the Group VI metal compound are in the form of oxides.

5

The catalyst according to the invention is prepared as follows:

10 The starting material is a conventional hydrotreating catalyst comprising a Group VIII metal oxide component and a Group VI metal oxide component on a carrier.

As Group VI metals may be mentioned molybdenum, tungsten, and chromium. Group VIII metals include nickel, cobalt, and iron. Especially preferred in this connection is a combination of nickel and/or cobalt and molybdenum and/or tungsten. If the hydrodesulphurisation activity of the catalyst is the more
15 important, a combination of cobalt and molybdenum is advantageous. If the hydrodenitrogenation activity of the catalyst is the more important, a combination of nickel and molybdenum or tungsten is advantageous. The catalyst usually has a metal content in the range of 0,1 to 50 wt.%, calculated on the overall weight of the catalyst.
20 The Group VI and Group VIII metals will frequently be present in amounts of 5-30 wt.% and 1-10 wt.%, respectively, calculated as trioxide and monoxide, respectively, the two amounts being calculated on the overall weight of the catalyst. If so desired, the catalyst may also contain other components, such as phosphorus,
25 halogens, and borium. Particularly, the presence of phosphorus in an amount of 1-10 wt.%, calculated as P_2O_5 , to improve the hydrodenitrogenation activity of the catalyst is preferred.

30 The catalyst carrier may be composed of the conventional oxides, e.g., alumina, silica, silica-alumina, alumina with silica-alumina dispersed therein, silica-coated alumina, magnesia, zirconia, boria, and titania, as well as mixtures of these oxides. As a rule,

preference is given to the carrier being of alumina, silica-alumina, alumina with silica-alumina dispersed therein, or silica-coated alumina. Special preference is given to alumina and alumina containing up to 10 wt.% of silica. A carrier containing a transition alumina, for example an eta, theta, or gamma alumina is preferred within this group, wherein a gamma-alumina carrier is most especially preferred.

The catalyst's pore volume (measured via mercury penetration) is not critical to the process according to the invention and will generally be in the range of 0,5 to 1 ml/g. The specific surface area is not critical to the process according to the invention either and will generally be in the range of 50 to 400 m²/g (measured using the BET method). Preferably, the catalyst will have a median pore diameter in the range of 7-15 nm, as determined by mercury porosimetry, and at least 60% of the total pore volume will be in the range of ± 2 nm from the median pore diameter.

The catalyst is employed in the conventional manner in the form of spheres or extrudates. Examples of suitable types of extrudates have been disclosed in the literature (see, int. al., US 4 028 227). Highly suitable for use are cylindrical particles (which may be hollow or not) as well as symmetrical and asymmetrical polylobed particles (2, 3 or 4 lobes).

The conventional hydrotreating catalysts suitable for use in the process according to the invention may be obtained, e.g., as follows. A carrier precursor is prepared, e.g., in the case of alumina, in the form of an alumina hydrogel (boehmite). After it has been dried or not, e.g., by means of spray-drying, it is shaped into particles, for example by extrusion. The shaped particles are calcined at a temperature in the range of 400° to 850°C, resulting, in the case of alumina, in a carrier containing a transition

alumina, e.g., a gamma, theta, or eta-alumina. Then, suitable amounts of precursors for the hydrogenation metals and the optional other components, such as phosphorus, are deposited on the catalyst, for example in the form of an aqueous solution. In the case of Group VI metals and Group VIII metals, the precursors may be ammonium molybdate, ammonium tungstenate, cobalt nitrate and/or nickel nitrate. Suitable phosphorus component precursors include phosphoric acid and the various ammonium hydrogen phosphates.

After an optional drying step at a temperature in the range of 25°-200°C, the resulting material is calcined at a temperature in the range of 350°-750°C to convert the metal component precursors, and the optional other component precursors to form oxide components.

It will be clear to the skilled man that there can be a wide number of variations on this method. Thus, it is possible to apply a plurality of impregnating steps, the impregnating solutions to be used containing one or more of the component precursors that are to be deposited, or a portion thereof. Instead of impregnating techniques there can be used dipping methods, spraying methods, etc. With multiple impregnation, dipping, etc. drying and/or calcining may be carried out in between. Alternatively, one or more component precursors can be mixed wholly or in part with the carrier prior to the shaping step being carried out. In such an embodiment the component precursor material, or a portion thereof, can be deposited on the not yet shaped carrier material, say, a powder, by means of, e.g., impregnation, after which the shaping step is carried out. Alternatively, it is possible to intimately mix one or more component precursors wholly or in part with the carrier material during the shaping step rather than prior to it. Techniques that are suitable for this process are co-pelletisation and co-extrusion. It is recommended that the group VIB metal component precursor employed in this process be molybdenum trioxide.

Conventional hydrotreating catalysts and the processes for preparing them are described in, e.g., US 4 738 767, US 4 062, 809, US 4 500 424, GB 1 504 586, US 4 212 729, US 4 326 995, US 4 051 021, US 4 066 574, EP-A 0 469 675.

5

As stated before, the process according to the invention includes both the activation of fresh hydrotreating catalyst prepared for the process, and the activation of hydrotreating catalyst which has been used and regenerated.

10

15

The conventional hydrotreating catalyst used as starting material is impregnated with an impregnation solution comprising the selected additive in an appropriate solvent. The solvent used in preparing the additive impregnation solution generally is water, although other compounds, such as methanol, ethanol, and other alcohols may also be suitable, depending on the nature of the additive.

20

The additive to be used in preparing the catalyst according to the invention is selected from the group of compounds comprising at least two hydroxyl groups and 2-10 carbon atoms per molecule, and the (poly)ethers of these compounds. It is possible to use a single compound or a combination of compounds.

25

Suitable compounds for use in the process according to the invention include aliphatic alcohols such as ethylene glycol, propylene glycol, glycerin, trimethylol ethane, trimethylol propane, etc.

30

Ethers of these compounds include diethylene glycol, dipropylene glycol, trimethylene glycol, triethylene glycol, tributylene glycol, tetraethylene glycol, tetrapentylene glycol. This range can be extrapolated to include polyethers like polyethylene glycol. For this last compound, polyethylene glycol with a molecular weight between 200 and 600 is preferred.

Other ethers which are suitable for use in the present invention include ethylene glycol monobutyl ether, diethylene glycol

monomethyl ether, diethylene glycol monoethyl ether, diethylene glycol monopropyl ether, and diethylene glycol monobutyl ether.

Another group of compounds comprising at least two hydroxyl groups and 2-10 carbon atoms per molecule are the saccharides. Preferred
5 saccharides include monosaccharides such as glucose and fructose. Ethers thereof include disaccharides such as lactose, maltose, and saccharose. Polyethers of these compounds include the polysaccharides.

10 The amount of additive to be used depends on the specific situation. An important factor in deciding both the suitability of the additive as such and the amount of additive to be used is the viscosity of the impregnation solution containing the additive.

In order for the process according to the invention to be a success,
15 the additive must be distributed homogeneously over the catalyst. This is suitably effected by impregnating the catalyst with an impregnation solution comprising the additive in a solvent, with the total volume of the impregnation solution being in the range of the total pore volume of the catalyst to be impregnated.

20 In this technique, which is known in the art as pore volume impregnation, the impregnation solution will be taken up virtually completely by the pores of the catalyst, which makes for an efficient use of chemicals. If the impregnation solution is too viscous, the impregnation step will not result in a homogeneous
25 distribution of the additive over the catalyst.

It was found that the appropriate amount of additive generally lies in the range of 0.01-2.5 moles of additive per mole of hydrogenation metals present in the catalyst. If the amount of additive added is too low, the advantageous effect of the present invention will not
30 be obtained. On the other hand, the addition of an exceptionally large amount of additive will not improve the effect of the present invention. On the contrary, besides being a waste of material, the addition of more additive than necessary results in a large quantity

of organic materials being present in the catalyst, which may lead to detrimental coke formation when the catalyst is used. Further, as has been explained before, the use of a large quantity of additive may increase the viscosity of the impregnation solution to an unacceptable value. As will be clear to the person skilled in the art, the exact amount of additive to be used in a specific situation, and the upper and lower limits for these ranges, will depend upon a variety of parameters including the metals content of the catalyst, the pore volume and pore size distribution of the catalyst, the nature of the additive, the solvent to be used in the impregnation solution, the impregnation conditions, etc. It is well within the scope of the person skilled in the art to determine the optimum amount of additive to be used in each specific situation, taking the above-mentioned variables into account.

The viscosity of the additive at room temperature may give some indication of the amount of additive which may suitably be used in the process according to the invention, with the general trend being the more viscous the additive, the less of it can be incorporated into the catalyst. The following Table gives the viscosity at room temperature, the generally preferred range, and the more preferred range for various additives which may be used in the process according to the invention.

	Additive	Viscosity (20°C) cps	Amount (mole/mole)	
			General	Preferred
5	ethylene glycol monobutyl ether	3	0.01-2.5	0.05-1.5
	diethylene glycol monomethyl ether	4	0.01-2.5	0.05-1.5
	diethylene glycol monoethyl ether	4	0.01-2.5	0.05-1.5
	diethylene glycol monopropyl ether	5	0.01-2.5	0.05-1.5
	diethylene glycol monobutyl ether	6	0.01-2.5	0.05-1.5
10	ethylene glycol	21	0.01-2.5	0.05-1.5
	propylene glycol	56	0.01-2.0	0.05-1.0
	diethylene glycol	38	0.01-2.0	0.05-1.0
	trimethylene glycol	56	0.01-2.0	0.05-1.0
	triethylene glycol	48	0.01-2.0	0.05-1.0
15	tetraethylene glycol	58	0.01-2.0	0.05-1.0
	polyethylene glycol (MW200)	61	0.01-2.0	0.05-1.0
	polyethylene glycol (MW400)	100	0.01-1.5	0.05-0.8
	polyethylene glycol (MW600)	140	0.01-1.5	0.05-0.8
	glycerin	1500	0.01-1.5	0.05-0.8
20	trimethylol ethane	solid	0.01-1.5	0.05-0.5
	trimethylol propane	solid	0.01-1.5	0.05-0.5
	glucose	solid	0.01-1.5	0.05-0.5
	fructose	solid	0.01-1.5	0.05-0.5
	maltose	solid	0.01-1.5	0.05-0.5
25	lactose	solid	0.01-1.5	0.05-0.5
	saccharose	solid	0.01-1.5	0.05-0.5

25 The impregnation step, which is generally carried out according to the pore volume impregnation technique described before, merely comprises adding the impregnation solution to the catalyst particles and homogenising the mixture until virtually all of the impregnation solution is taken up into the catalyst. The technique of

30 impregnation is well-known to the person skilled in the art of hydrotreating catalysts.

After the impregnation step has been completed, the catalyst is dried to remove the solvent. It is essential to the process according to the invention that the drying step is effected in such a manner that the additive remains in the catalyst and is not removed by evaporation or decomposition. In consequence, the drying conditions to be applied depend heavily on the temperature at which the specific additive boils or decomposes. In the context of the present invention, the drying step should be carried out under such conditions that at least 50%, preferably 70 %, more preferably 90% of the additive which was incorporated into the catalyst in the impregnation step is still present in the catalyst after the drying step. Of course, it is preferred to keep as much additive as possible in the catalyst during the drying step, but with the more volatile additives additive evaporation during the drying step cannot always be avoided. The drying step may, e.g., be carried out in air, under vacuum, or in inert gas. Generally, it is advantageous to have a drying temperature below 220°C, although a lower temperature may be necessary, depending on the nature of the additive.

It is not altogether clear what causes the surprisingly high hydrotreating activity of the hydrotreating catalyst according to the invention. It may be that the improvement in activity is caused by the fact that the additive somehow prevents aggregation of the metal compound during the sulphide formation, which leads both to an easy sulphidation without the necessity of adding additional sulphur components and to a high activity.

It has been found that it is preferred for the catalyst according to the invention to show a peak in its X-ray diffraction pattern at $2\theta = 6-8^\circ$. It appears that catalysts according to the invention which show this peak are more active than catalysts according to the invention which do not show this peak.

The dried additive-containing hydrotreating catalyst may be subjected to a sulphiding step before it is used in the hydrotreating of hydrocarbon feeds, but, as has been explained before, this is not necessary.

5 If it is decided to sulphide the catalyst before use, this can be done in one of the ways known in the art. For example, it is possible to contact the catalyst with inorganic or organic sulphur compounds, such as hydrogen sulphide, elemental sulphur, or organic polysulphides, or to sulphide the catalyst by contacting it with a
10 hydrocarbon feed to which a sulphur compound has been added. All of this will be known to the skilled person as catalyst sulphiding or presulphiding.

15 The present catalysts can be used in the hydrotreating of a wide range of feeds. Examples of suitable feeds include middle distillates, kero, naphtha, vacuum gas oils, and heavy gas oils.

20 The conventional process conditions, such as temperatures in the range of 250°-450°C, pressures in the range of 5-250 bar, space velocities in the range of 0,1-10 hr⁻¹, and H₂/oil ratios in the range of 50-2000 Nl/l, can be applied here.

Examples

25 Example 1: Preparation of a hydrodesulphurisation catalyst using ethylene glycol

30 Comparative catalyst A, which is to be used as starting material, is prepared as follows. One kilogram of gamma-alumina extrudates is impregnated with an aqueous impregnation solution containing suitable amounts of molybdenum trioxide, cobalt carbonate, and phosphoric acid. The impregnated extrudates are dried for 16 hours at 100°C, after which the dried extrudates are calcined for three

hours at 400°C in air. The thus obtained catalyst contained 22 wt.% of molybdenum, calculated as trioxide, 3 wt.% of cobalt, calculated as oxide, and 4 wt.% of phosphorus, calculated as P₂O₅.

5 Various catalysts according to the invention were prepared by impregnating Comparative catalyst A to pore volume saturation with an impregnation solution comprising an appropriate amount of ethylene glycol mixed in water, to obtain the amount of ethylene glycol in the catalyst composition given in Table 2. The catalysts
10 were then dried under the conditions given in Table 2.

In the Examples of the present specification the various catalysts according to the invention will be indicated by codes consisting of two letters and a numeral. The first letter stands for the catalyst
15 used as starting material. The second letter is intended to identify the additive used. The numeral indicates the number of the Experiment within a certain series.

Comparative catalysts which do not contain any additive are
20 indicated with the letter indicating the starting material, followed by the number of the treatment and a C in parentheses to indicate that it is a comparative example. Comparative catalysts which do contain additive but which are otherwise not according to the invention are indicated with a letter indicating the starting
25 catalyst, a letter indicating the additive, and a numeral indicating the number of the experiment, followed by a C in parentheses. The starting comparative catalyst A is indicated as A(C).

Comparative catalyst A1(C) was prepared by impregnating Comparative
30 catalyst A to pore volume saturation with water, and then drying the resulting product for 16 hours at 100°C.

Comparative Catalyst A2(C) was prepared by sulphiding Comparative catalyst A with TNPS, as is described in Japanese patent publication

No. H-4 79701.

Comparative catalyst AA1(C) was prepared by subjecting a catalyst with the same composition as Catalyst AA2 to a calcination step.

5 Comparative catalyst AA2(C) was prepared by a process in which a too large amount of additive was used as compared with the amount of metal present. The presence of a too large amount of additive will cause plugging of the catalyst pores with additive, detrimentally affecting activity.

10 Comparative catalyst AA3(C) was prepared by a process in which the catalyst is dried at a temperature which is so high that at least a substantial part of the additive decomposes or evaporates.

15 The X-ray diffraction pattern of the various catalysts was determined using a Rotaflex RAD-rVB made by Rigaku Electric Co. Ltd., using a copper X-ray diffraction vessel with a vessel voltage of 40kV, at 150 mA, with a divergence slit of 1° and a light emission slit of 0.3 mm.

In Table 2 it is indicated which of the catalysts show a peak in the X-ray diffraction pattern at $2\theta=6-8^\circ$.

20 To be tested, 15 ml of each catalyst was brought into a continuous reactor and tested using two kinds of feeds:

Feed A: Kuwait straight-run light gas oil (LGO) containing 1.15 wt.% of sulphur and 68 ppm of nitrogen

25 Feed B: Feed A to which 3% butane diol had been added.

First, each catalyst was presulphided under the conditions given below, with the presulphiding being directly followed by catalyst testing.

Table 1: Presulphiding and test conditions

	Presulphiding	Testing
5		
Temperature (°C)	316	330
H ₂ pressure (kg/cm ²)	20	30
LHSV (hr ⁻¹)	1	2
H ₂ /feed ratio (Nl/l)	200	300
10		
Time (hours)	18	168

The relative volume activities for the various catalysts were determined as follows. For each catalyst the reaction constant k_n was calculated from the following formula:

$$15 \quad k_n = \text{LHSV} \times 1/(n-1) \times (1/S^{n-1} \times 1/S_0^{n-1})$$

in which the S stands for the percentage of sulphur in the product, S_0 stands for the percentage of sulphur in the feed, and n stands for the reaction order of the hydrodesulphurisation reaction. In the present experiments, n has the value 1.75.

The reaction constant of Comparative catalyst A was set at 100, and the reaction constants of the other catalysts were recalculated to obtain the relative volume activities. The results for both feed A and feed B are given in Table 2.

The percentage of sulphur present in the feed and in the product was determined using an SLFA-920 of Horiba Manufacturing Co., Ltd.

Table 2:

	Catalyst	Additive (mole/mole)	Drying		Calcining		X-ray	Activity	
			T	t	T	t		A	B
			(°C)	(hr)	(°C)	(hr)			
10	AA1	0.05	100	16	-	-	+	167	168
	AA2	0.25	100	16	-	-	+	168	171
	AA3	1.00	100	16	-	-	+	172	175
15	A(C)	-	-	-	-	-	-	100	126
	A1(C)	0	100	16	-	-	+	98	122
	A2(C)	-	-	-	-	-	-	123	127
	AA1(C)	0.25	100	16	500	4	-	101	128
	AA2(C)	3.00	100	16	-	-	+	98	125
	AA3(C)	0.25	300	16	-	-	+	108	128

From Table 2 it is clear that the catalysts according to the invention show a higher activity than the ones which are not according to the invention. The catalyst according to the invention which is not subjected to a separate sulphiding step appears to show a higher activity even than the sulphided conventional catalyst A2(C).

Example 2: Preparation of a hydrodesulphurisation catalyst using diethylene glycol monoethyl ether

Further catalysts according to the invention and comparative catalysts were prepared using diethylene glycol monoethyl ether as additive. Again, the additive was mixed with appropriate amounts of water to impregnate the catalyst by way of pore volume impregnation.

The catalysts were presulphided and tested in the manner described in Example 1. Catalyst composition and test results are summarised in Table 3.

5 Table 3:

	Catalyst	Additive (mole/mole)	Drying		Calcining		X-ray	Activity	
			T (°C)	t (hr)	T (°C)	t (hr)		A	B
10	AB1	0.05	100	16	-	-	+	161	165
	AB2	0.25	100	16	-	-	+	156	161
	AB3	1.00	100	16	-	-	+	161	165
15	A(C)	-	-	-	-	-	-	100	126
	A1(C)	0	100	16	-	-	+	98	122
	A3(C)	-	-	-	-	-	-	123	127
	AB1(C)	0.25	100	16	500	4	-	97	124
	AB2(C)	3.00	100	16	-	-	+	96	124
20	AB3(C)	0.25	300	16	-	-	+	110	127

Again, the catalysts according to the invention show a much higher activity than the comparative catalysts in the hydrodesulphurisation of both Feed A and Feed B.

25

Example 3: Preparation of a hydrodesulphurisation catalyst using polyethylene glycol (MW200)

30

Example 1 was repeated, except that a polyethylene glycol with an average molecular weight of 200 was used as additive. The additive was mixed with appropriate amounts of water to impregnate the catalysts by way of pore volume impregnation. The catalysts were

presulphided and tested in the manner described in Example 1. Catalyst composition and test results are summarised in Table 4.

Table 4:

	Catalyst	Additive (mole/mole)	Drying		Calcining		X-ray	Activity	
			T (°C)	t (hr)	T (°C)	t (hr)		A	B
5									
10	AC1	0.05	100	16	-	-	+	166	168
	AC2	0.25	100	16	-	-	+	164	165
	AC3	1.00	100	16	-	-	+	161	168
15	A(C)	-	-	-	-	-	-	100	126
	A1(C)	0	100	16	-	-	+	98	122
	A3(C)	-	-	-	-	-	-	123	127
	AC1(C)	0.25	100	16	500	4	-	102	130
	AC2(C)	3.00	100	16	-	-	+	93	123
20	AC3(C)	0.25	300	16	-	-	+	105	127

Again, the catalysts according to the invention show a much higher activity than the comparative catalysts in the hydrodesulphurisation of both Feed A and Feed B.

25

Example 4: Preparation of a hydrodesulphurisation catalyst using diethylene glycol

30

Example 1 was repeated, except that diethylene glycol was used as additive. The additive was mixed with appropriate amounts of water to impregnate the catalysts by way of pore volume impregnation. The catalysts were presulphided and tested in the manner described in

Example 1. Catalyst composition and test results are summarised in Table 5.

Table 5:

Catalyst	Additive (mole/mole)	Drying		Calcining		X-ray	Activity	
		T (°C)	t (hr)	T (°C)	t (hr)		A	B
AD1	0.05	100	16	-	-	+	174	178
AD2	0.25	100	16	-	-	+	174	184
AD3	1.00	100	16	-	-	+	173	175
A(C)	-	-	-	-	-	-	100	126
A1(C)	0	100	16	-	-	+	98	122
A3(C)	-	-	-	-	-	-	123	127
AD1(C)	0.25	100	16	500	4	-	103	130
AD2(C)	3.00	100	16	-	-	+	100	129
AD3(C)	0.25	300	16	-	-	+	108	128

Again, the catalysts according to the invention show a much higher activity than the comparative catalysts in the hydrodesulphurisation of both Feed A and Feed B.

Example 5: Preparation of a hydrodesulphurisation catalyst using polyethylene glycol (MW400)

Example 1 was repeated, except that a polyethylene glycol with an average molecular weight of 400 was used as additive. The additive was mixed with appropriate amounts of water to impregnate the catalysts by way of pore volume impregnation. The catalysts were

presulphided and tested in the manner described in Example 1. Catalyst composition and test results are summarised in Table 6.

Table 6:

Catalyst	Additive (mole/mole)	Drying		Calcining		X-ray	Activity	
		T (°C)	t (hr)	T (°C)	t (hr)		A	B
AE1	0.05	100	16	-	-	+	154	158
AE2	0.25	100	16	-	-	+	149	156
AE3	1.00	100	16	-	-	+	151	155
A(C)	-	-	-	-	-	-	100	126
A1(C)	0	100	16	-	-	+	98	122
A3(C)	-	-	-	-	-	-	123	127
AE1(C)	0.25	100	16	500	4	-	100	125
AE2(C)	3.00	100	16	-	-	+	89	119
AE3(C)	0.25	300	16	-	-	+	103	123

Again, the catalysts according to the invention show a much higher activity than the comparative catalysts in the hydrodesulphurisation of both Feed A and Feed B.

Example 6: Preparation of a hydrodesulphurisation catalyst using trimethylol ethane

Example 1 was repeated, except that trimethylol ethane was used as additive. The additive was mixed with appropriate amounts of water to impregnate the catalysts by way of pore volume impregnation. The catalysts were presulphided and tested in the manner described in

Example 1. Catalyst composition and test results are summarised in Table 7.

Table 7:

5	Catalyst	Additive (mole/mole)	Drying		Calcining		X-ray	Activity	
			T (°C)	t (hr)	T (°C)	t (hr)		A	B
10	AF1	0.05	100	16	-	-	+	146	149
	AF2	0.25	100	16	-	-	+	148	149
	AF3	1.00	100	16	-	-	+	143	145
15	A(C)	-	-	-	-	-	-	100	126
	A1(C)	0	100	16	-	-	+	98	122
	A3(C)	-	-	-	-	-	-	123	127
	AF1(C)	0.25	100	16	500	4	-	97	126
	AF2(C)	3.00	100	16	-	-	+	88	120
20	AF3(C)	0.25	300	16	-	-	+	103	126

- Again, the catalysts according to the invention show a much higher activity than the comparative catalysts in the hydrodesulphurisation of both Feed A and Feed B.

Example 7: Preparation of a hydrodesulphurisation catalyst using glucose

Example 1 was repeated, except that glucose was used as additive. The additive was mixed with appropriate amounts of water to impregnate the catalysts by way of pore volume impregnation. The catalysts were presulphided and tested in the manner described in Example 1. Catalyst composition and test results are summarised in Table 8.

Table 8:

	Catalyst	Additive (mole/mole)	Drying		Calcining		X-ray	Activity	
			T (°C)	t (hr)	T (°C)	t (hr)		A	B
15	AG1	0.05	100	16	-	-	+	142	148
	AG2	0.25	100	16	-	-	+	148	146
20	AG3	1.00	100	16	-	-	+	141	145
	A(C)	-	-	-	-	-	-	100	126
	A1(C)	0	100	16	-	-	+	98	122
	A3(C)	-	-	-	-	-	-	123	127
25	AG1(C)	0.25	100	16	500	4	-	100	125
	AG2(C)	3.00	100	16	-	-	+	79	111
	AG3(C)	0.25	300	16	-	-	+	105	124

Again, the catalysts according to the invention show a much higher activity than the comparative catalysts in the hydrodesulphurisation of both Feed A and Feed B.

Example 8: Preparation of a hydrodenitrogenation catalyst using ethylene glycol

Comparative catalyst B, which is to be used as starting material for hydrodenitrogenation catalysts, is prepared as follows. One kilogram of gamma-alumina extrudates is impregnated with an aqueous impregnation solution containing suitable amounts of molybdenum trioxide, nickel carbonate, and phosphoric acid. The impregnated extrudates are dried for 16 hours at 100°C, after which the dried extrudates are calcined for four hours at 500°C in air. The thus obtained catalyst contained 18 wt.% of molybdenum, calculated as trioxide, 4 wt.% of nickel, calculated as oxide, and 6 wt.% of phosphorus, calculated as P₂O₅.

Various catalysts according to the invention were prepared by impregnating Comparative catalyst B to pore volume saturation with an impregnation solution comprising an appropriate amount of ethylene glycol mixed in water, to obtain the amount of ethylene glycol in the catalyst composition given in Table 9. The catalysts were then dried under the conditions given in Table 9.

The starting Comparative catalyst B is indicated as B(C). Comparative catalyst B1(C) was prepared by impregnating Comparative catalyst B to pore volume saturation with water, and then drying the resulting product for 16 hours at 100°C.

Comparative catalyst B2(C) was prepared by sulphiding Comparative catalyst B with TNPS, as is described in Japanese patent publication No. H-4 79701.

Comparative catalyst BA1(C) was prepared by subjecting a catalyst with the same composition as Catalyst BA2 to a calcination step.

Comparative catalyst BA2(C) was prepared by a process in which a too large amount of additive was used as compared with the amount of metal present. The presence of a too large amount of additive will

cause plugging of the catalyst pores with additive, detrimentally affecting activity.

Comparative catalyst BA3(C) was prepared by a process in which the catalyst is dried at a temperature which is so high that at least part of the additive decomposes or evaporates.

To be tested, 15 ml of each catalyst was brought into a continuous reactor and tested using the feed types also applied in the hydrodesulphurisation experiments described before. The catalysts were presulphided and used under the same conditions as applied for the hydrodesulphurisation experiments described before. Reference is made to Table 1 in Example 1.

The reaction velocity was calculated from the quantity of nitrogen in the product in relation to the quantity of nitrogen in the feed. The quantity of nitrogen was determined using a TN-5 nitrogen analyser of Misubishi Kasei. The velocity constant was calculated using the pseudolinear formula 2, in which N_0 stands for the amount of nitrogen present in the feed, while N stands for the amount of nitrogen present in the product.

$$k_n = LHSV \times \ln(N_0/N)$$

The activity of comparative catalyst B is set at 100, and the values found for the other catalysts are recalculated in relation to this value. The results obtained for the various catalysts in the hydrodenitrogenation of both Feed A and Feed B are given in Table 9.

Table 9:

	Catalyst	Additive (mole/mole)	Drying		Calcining		X-ray	Activity	
			T (°C)	t (hr)	T (°C)	t (hr)		A	B
5	BA1	0.05	100	16	-	-	+	174	179
	BA2	0.25	100	16	-	-	+	178	182
	BA3	1.00	100	16	-	-	+	181	180
10	B(C)	-	-	-	-	-	-	100	148
	B1(C)	0	100	16	-	-	+	97	154
	B2(C)	-	-	-	-	-	-	150	149
	BA1(C)	0.25	100	16	500	4	-	149	150
15	BA2(C)	3.00	100	16	-	-	+	114	148
	BA3(C)	0.25	300	16	-	-	+	98	146

From the values given in Table 9 it is clear that the catalysts according to the invention show a much higher activity for the hydrodenitrogenation of both Feed A and Feed B than the comparative catalysts. This goes for the comparative catalysts which were prepared without the use of an additive as well as for the catalysts which were prepared using an additive but in which the additive was either removed by calcination (BA1(C)), or in which too much additive was used (BA2(C)), or in which the additive was removed by drying at a too high temperature (BA3(C)).

Example 9: Preparation of a hydrodenitrogenation catalyst using diethylene glycol monoethyl ether

Example 8 was repeated, except that diethylene glycol monoethyl ether was used as additive. The additive was mixed with appropriate amounts of water to impregnate the catalysts by way of pore volume

impregnation. The catalysts were presulphided and tested in the manner described in Example 8. Catalyst composition and test results are summarised in Table 10.

5 Table 10:

Catalyst	Additive (mole/mole)	Drying		Calcining		X-ray	Activity	
		T (°C)	t (hr)	T (°C)	t (hr)		A	B
10 BB1	0.05	100	16	-	-	+	192	194
BB2	0.25	100	16	-	-	+	190	189
BB3	1.00	100	16	-	-	+	193	192
15 B(C)	-	-	-	-	-	-	100	148
B1(C)	0	100	16	-	-	+	112	154
B3(C)	-	-	-	-	-	-	148	150
BB1(C)	0.25	100	16	500	4	-	101	150
20 BB2(C)	3.00	100	16	-	-	+	114	143
BB3(C)	0.25	300	16	-	-	+	104	147

It is clear that the catalysts according to the invention show much higher activity in the hydrogenation of the two feeds than the comparative catalysts.

25 Example 10: Preparation of a hydrodenitrogenation catalyst using polyethylene glycol (MW 200)

30 Example 8 was repeated, except that a polyethylene glycol with a molecular weight of 200 was used as additive. The additive was mixed with appropriate amounts of water to impregnate the catalysts by way of pore volume impregnation. The catalysts were presulphided and

tested in the manner described in Example 8. Catalyst composition and test results are summarised in Table 11.

Table 11:

	Catalyst	Additive (mole/mole)	Drying		Calcining		X-ray	Activity	
			T (°C)	t (hr)	T (°C)	t (hr)		A	B
5									
10	BC1	0.05	100	16	-	-	+	177	181
	BC2	0.25	100	16	-	-	+	185	186
	BC3	1.00	100	16	-	-	+	186	188
15	B(C)	-	-	-	-	-	-	100	148
	B1(C)	0	100	16	-	-	+	112	154
	B3(C)	-	-	-	-	-	-	148	150
	BC1(C)	0.25	100	16	500	4	-	98	145
	BC2(C)	3.00	100	16	-	-	+	110	138
20	BC3(C)	0.25	300	16	-	-	+	98	143

It is clear that the catalysts according to the invention show much higher activity in the hydrogenation of the two feeds than the comparative catalysts.

25 Example 11: Preparation of a hydrodenitrogenation catalyst using diethylene glycol

30 Example 8 was repeated, except that diethylene glycol was used as additive. The additive was mixed with appropriate amounts of water to impregnate the catalysts by way of pore volume impregnation. The catalysts were presulphided and tested in the manner described in

Example 8. Catalyst composition and test results are summarised in Table 12.

Table 12:

	Catalyst	Additive (mole/mole)	Drying		Calcining		X-ray	Activity	
			T (°C)	t (hr)	T (°C)	t (hr)		A	B
5									
10	BD1	0.05	100	16	-	-	+	201	205
	BD2	0.25	100	16	-	-	+	205	208
	BD3	1.00	100	16	-	-	+	201	203
15	B(C)	-	-	-	-	-	-	100	148
	B1(C)	0	100	16	-	-	+	112	154
	B3(C)	-	-	-	-	-	-	148	150
	BD1(C)	0.25	100	16	500	4	-	102	151
	BD2(C)	3.00	100	16	-	-	+	128	153
20	BD3(C)	0.25	300	16	-	-	+	107	149

It is clear that the catalysts according to the invention show much higher activity in the hydrogenation of the two feeds than the comparative catalysts.

Example 12: Preparation of a hydrodenitrogenation catalyst using polyethylene glycol (MW 400)

Example 8 was repeated, except that a polyethylene glycol with an average molecular weight of 400 was used as additive. The additive was mixed with appropriate amounts of water to impregnate the catalysts by way of pore volume impregnation. The catalysts were

presulphided and tested in the manner described in Example 8. Catalyst composition and test results are summarised in Table 13.

Table 13:

	Catalyst	Additive (mole/mole)	Drying		Calcining		X-ray	Activity	
			T (°C)	t (hr)	T (°C)	t (hr)		A	B
5									
10	BE1	0.05	100	16	-	-	+	184	188
	BE2	0.25	100	16	-	-	+	190	192
	BE3	1.00	100	16	-	-	+	186	190
15	B(C)	-	-	-	-	-	-	100	148
	B1(C)	0	100	16	-	-	+	112	154
	B3(C)	-	-	-	-	-	-	148	150
	BE1(C)	0.25	100	16	500	4	-	100	145
	BE2(C)	3.00	100	16	-	-	+	121	152
20	BE3(C)	0.25	300	16	-	-	+	104	147

It is clear that the catalysts according to the invention show much higher activity in the hydrogenation of the two feeds than the comparative catalysts.

Example 13: Preparation of a hydrodenitrogenation catalyst using trimethylol ethane

Example 8 was repeated, except that trimethylol ethane was used as additive. The additive was mixed with appropriate amounts of water to impregnate the catalysts by way of pore volume impregnation. The catalysts were presulphided and tested in the manner described in

Example 8. Catalyst composition and test results are summarised in Table 14.

Table 14:

	Catalyst	Additive (mole/mole)	Drying		Calcining		X-ray	Activity	
			T (°C)	t (hr)	T (°C)	t (hr)		A	B
5									
10	BF1	0.05	100	16	-	-	+	170	172
	BF2	0.25	100	16	-	-	+	175	176
	BF3	1.00	100	16	-	-	+	177	181
15	B(C)	-	-	-	-	-	-	100	148
	B1(C)	0	100	16	-	-	+	112	154
	B3(C)	-	-	-	-	-	-	148	150
	BF1(C)	0.25	100	16	500	4	-	100	150
	BF2(C)	3.00	100	16	-	-	+	94	143
20	BF3(C)	0.25	300	16	-	-	+	99	149

Again, the catalysts according to the invention show much higher activity in the hydrogenation of the two feeds than the comparative catalysts.

25

Example 14: Preparation of a hydrodenitrogenation catalyst using glucose

30

Example 8 was repeated, except that glucose was used as additive. The additive was mixed with appropriate amounts of water to impregnate the catalysts by way of pore volume impregnation. The catalysts were presulphided and tested in the manner described in

Example 8. Catalyst composition and test results are summarised in Table 15.

Table 15:

5	Catalyst	Additive (mole/mole)	Drying		Calcining		X-ray	Activity	
			T (°C)	t (hr)	T (°C)	t (hr)		A	B
10	BG1	0.05	100	16	-	-	+	169	171
	BG2	0.25	100	16	-	-	+	165	169
	BG3	1.00	100	16	-	-	+	165	167
15	B(C)	-	-	-	-	-	-	100	148
	B1(C)	0	100	16	-	-	+	112	154
	B3(C)	-	-	-	-	-	-	148	150
	BG1(C)	0.25	100	16	500	4	-	97	149
	BG2(C)	3.00	100	16	-	-	+	98	141
20	BG3(C)	0.25	300	16	-	-	+	96	145

It is clear that the catalysts according to the invention show much higher activity in the hydrogenation of the two feeds than the comparative catalysts.

CLAIMS

1. A process for activating a hydrotreating catalyst comprising a Group VIII hydrogenation metal oxide and a Group VI hydrogenation metal oxide on a carrier in which the hydrotreating catalyst is contacted with an additive which is at least one compound selected from the group of compounds comprising at least two hydroxyl groups and 2-10 carbon atoms, and the (poly)ethers of these compounds, after which the catalyst is dried under such conditions that at least 50% of the additive remains in the catalyst.
2. A process according to claim 1 wherein the additive is at least one compound selected from ethylene glycol, diethylene glycol, and polyethylene glycol.
3. A process according to claim 1 wherein the additive is a saccharide or a polysaccharide.
4. A process according to any one of the preceding claims wherein the mole ratio between the amount of additive and the amount of hydrogenation metals is 0.01:1 to 2.5:1.
5. A process according to any one of the preceding claims wherein the hydrotreating catalyst to be activated is a fresh hydrotreating catalyst.
6. A process according to any one of claims 1 to 4 wherein the hydrotreating catalyst to be activated is a used hydrotreating catalyst which has been regenerated.
7. A process according to any one of the preceding claims wherein the hydrotreating catalyst to be activated comprises a

molybdenum oxide compound, an oxide compound of nickel or cobalt, and a phosphorus oxide compound on a carrier comprising gamma-alumina.

- 5 8. A hydrotreating catalyst obtainable by the process of any one of claims 1-7 which comprises a Group VIII metal oxide and a Group VI metal oxide on a carrier, which catalyst additionally comprises an additive which is at least one compound selected from the group of compounds comprising at least two hydroxyl groups and 2-10 carbon atoms, and the (poly)ethers of these compounds, wherein the Group VIII metal compound and the Group VI metal compound are in the form of oxides.
- 10
- 15 9. A hydrotreating catalyst according to claim 11, which shows a peak in its X-ray diffraction pattern at $2\theta = 6-8^\circ$.
- 20 10. A process for hydrotreating a hydrocarbon feed in which a hydrocarbon feed is contacted under hydrotreating conditions with a catalyst according to claim 8 or 9, which optionally has been (pre)sulphided before it is contacted with the hydrocarbon feed.
- 25 11. A process for hydrotreating a hydrocarbon feed according to claim 10, in which a catalyst according to claim 8 or 9 is contacted with a hydrocarbon feed containing at least 0.2 wt.% of S under hydrotreating conditions.
- 30

INTERNATIONAL SEARCH REPORT

International Application No

PCT/IB 96/00565

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C10G45/08 B01J23/85 B01J38/52

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 B01J C10G

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US,A,4 012 340 (MORIMOTO TATSUO) 15 March 1977 see column 3, line 51 - line 68 see column 7, line 64 - column 8, line 2 see claims; example 9 ---	1-11
X	EP,A,0 601 722 (SUMITOMO METAL MINING CO) 15 June 1994 cited in the application see page 3, line 30 - line 38 see page 3, line 52 - line 57 see page 5, line 1 - line 24 see page 7, line 1 - line 42 see claims ---	1-11
A	EP,A,0 382 588 (EURECAT EUROP RETRAIT CATALYS) 16 August 1990 -----	

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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INTERNATIONAL SEARCH REPORT

Information on patent family members

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